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(71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): HAYES, Paul, Michael [GB/GB]; 127 Church Street, Butt Lane, Kidsgrove, Stoke-on-Trent, Staffordshire ST7 1NX (GB). HODGSON, David, Ronald [GB/GB]; 7 Grenaby Avenue, Hinckley Green, Wigan, Merseyside WN2 4HZ (GB). MOCKFORD, Mary, Jane [GB/GB]; 19 Horrocks Road, Upton, Chester, Cheshire CH2 1HE (GB).			
(74) Agents: THOMAS, Ieuan et al.; ICI Chemicals & Polymers Ltd., Intellectual Property Dept., The Heath, P.O. Box 11, Runcom, Cheshire WA7 4QE (GB).			
(54) Title: PREPARATION OF ELECTRODE			
(57) Abstract			
<p>Preparation of an electrode comprising a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating thereon comprising at least an outer layer of an electrocatalytically-active material which comprises an oxide of at least ruthenium and an oxide of at least one non-noble metal by a one-step process which comprises the thermal spraying of a mixture of at least ruthenium and/or oxide thereof, at least one non-noble metal and/or oxide thereof, and preferably a second noble metal oxide, onto the substrate.</p>			

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PREPARATION OF ELECTRODE

This invention relates to a process for the preparation of an electrode for use in an electrolytic cell, and to the electrode prepared thereby, particularly to an electrode for use as an anode in an electrolytic cell, especially in an electrolytic cell in which in operation 5 chlorine is evolved at the anode, although use of the anode of the invention is not restricted to electrolyses in which chlorine is evolved.

Electrolytic processes are practised on a large scale throughout the world. For example, there are many industrial processes in which water or an aqueous solution is electrolysed, for example, an aqueous solution of an acid or an aqueous solution of an 10 alkali metal chloride. Aqueous acidic solutions are electrolysed in, for example, electrowinning, electrotinning and electrogalvanizing processes, and aqueous alkali metal chloride solutions are electrolysed in the production of chlorine and alkali-metal hydroxide, alkali metal hypochlorite, and alkali metal chlorate.

The production of chlorine and alkali metal hydroxide is practised in electrolytic 15 cells which comprise a mercury cathode or in electrolytic cells which comprise a plurality of alternating anodes and cathodes, which are generally of foraminous structure, arranged in separate anode and cathode compartments. These latter cells also comprise a separator, which may be a hydraulically permeable porous diaphragm or a substantially hydraulically impermeable ion-exchange membrane, positioned between adjacent anodes 20 and cathodes thereby separating the anode compartments from the cathode compartments, and the cells are also equipped with means for feeding electrolyte to the anode compartments and if necessary liquid to the cathode compartments, and with means for removing the products of electrolysis from these compartments. In a cell equipped with a porous diaphragm, aqueous, alkali metal chloride solution is charged to 25 the anode compartments of the cell, and chlorine is discharged from the anode compartments and hydrogen and cell-liquor containing alkali metal hydroxide are discharged from the cathode compartments of the cell. In a cell equipped with an ion-exchange membrane, aqueous alkali metal chloride solution is charged to the anode compartments of the cell and water or dilute aqueous alkali metal hydroxide solution to 30 the cathode compartments of the cell, and chlorine and depleted aqueous alkali metal chloride solution are discharged from the anode compartments of the cell and hydrogen and alkali metal hydroxide are discharged from the cathode compartments of the cell.

Electrolytic cells are also used in the electrolysis of non-aqueous electrolytes and in electrosynthesis.

It is desirable to operate such electrolytic cells at as low a voltage as possible in order to consume as little electrical power as possible and in such a way that the 5 component parts of the electrolytic cell are long lasting, ie the electrodes in the electrolytic cell should have a long lifetime.

In recent years anodes which have been used in such electrolytic processes have comprised a substrate of titanium or of an alloy of titanium possessing properties similar to those of titanium and a coating of an electrocatalytically-active material on the surface 10 of the substrate. An uncoated titanium anode could not be used in such an electrolytic process, the surface of the titanium would oxidise when anodically polarised and the titanium would soon cease to function as an anode. The use of such a coating of electrocatalytically-active material is essential in order that the titanium shall continue to function as an anode. Examples of such electrocatalytically-active materials which have 15 been used include metals of the platinum group, oxides of metals of the platinum group, mixtures of one or more such metals and one or more such oxides, and mixtures or solid solutions of one or more oxides of a platinum group metal and tin oxide or one or more oxides of a valve metal, that is one or more oxides of titanium, tantalum, zirconium, niobium, hafnium or tungsten.

20 Recently it has been suggested in EP 0,437,178 that anodes wherein the coating comprises mixed oxides of iridium, ruthenium and titanium having oxide molar ratios of Ti:(Ir + Ru) of less than 1:1 and of Ru:Ir of between 1.5:1 and 3:1 can be prepared from a certain acidic aqueous solution.

Likewise, it has been suggested in J 59,064788 that electrode coatings can be 25 prepared by the deposition of certain coatings from organic solvents followed by heating the coated substrate in oxygen.

We have now found surprisingly that electrodes for use in electrolytic cells may be prepared by thermal-spraying a mixture of powders of (i) a noble metal oxide, eg ruthenium oxide, and (ii) a suitable non-noble metal oxide onto a suitable substrate.

30 This process has the advantage compared with the processes known in the art that it affords a single-step coating process in the preparation of anodes.

The present invention provides a process for the preparation of an electrode which comprises a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating on the substrate which comprises at least an outer layer of electrocatalytically-active material and which, when used as an anode in an electrolytic cell in which chlorine is evolved at the anode, has an acceptable overvoltage.

According to the present invention there is provided a process for the preparation of an electrode which comprises a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating thereon comprising at least an outer layer of an electrocatalytically-active material which comprises an oxide of at least 10 ruthenium and an oxide of at least one non-noble metal which process comprises the step of thermal spraying a mixture of (i) at least ruthenium and/or oxide thereof and (ii) at least one non-noble metal and/or oxide thereof onto the substrate. Preferably the mixture which is thermal sprayed comprises a ruthenium oxide and at least one non-noble metal oxide.

As examples of thermal-spraying may be mentioned *inter alia* plasma spraying, high velocity oxy-fuel spraying (HVOF), oxy-acetylene spraying, wire spraying, and flame spraying.

As examples of suitable non-noble metals of which the mixture used in the process of the present invention may be comprised, particularly where it comprises a 20 plasma spraying process, may be mentioned *inter alia* tin and valve metals, eg titanium.

As examples of powders charged to the thermal spray gun in the process according to the present invention, particularly where the thermal spray-gun is a plasma spray-gun, may be mentioned *inter alia* an intimate mixture of particles of a ruthenium oxide and at least one non-noble metal oxide, particles of a solid solution of such oxides, 25 or particles of non-noble metal oxide bearing a coating of noble metal oxide thereon.

Where a plasma-spraying step is used in the process according to the present invention it is carried out in a reducing atmosphere and metal or metal alloy may be present in the coating produced on the substrate thereby.

We do not exclude the possibility that the electrode prepared by the process 30 according to the present invention may be subjected to a post heat-treatment in an oxidising atmosphere.

The possibility is not excluded of the coating of the electrode according to the present invention comprising one or more further layers intermediate the outer layer of the coating and the substrate, but it will be described hereinafter with reference to a coating which consists of only the aforementioned outer layer.

5 The layers in the coating are described as variously comprising an oxide of at least one noble metal and an oxide of at least one non-noble metal. Although the various oxides in the layers may be present as oxides per se it is to be understood that the oxides may together form a solid solution in which the oxides are not present as such. For example, the coating may comprise a solid solution of ruthenium dioxide and titanium
10 dioxide.

In general the electrode prepared by the process of the present invention will be used in the electrolysis of aqueous electrolytes and although the electrode of the invention is particularly suitable for use as an anode at which chlorine is evolved the electrode is not restricted to such use. It may, for example, be used as an anode in the
15 electrolysis of aqueous alkali metal chloride solution to produce alkali metal hypochlorite or alkali metal chlorate, or it may be used as an anode at which oxygen is evolved.

20 The substrate of the electrode comprises a valve metal or an alloy thereof having appropriate valve metal-like properties. Suitable valve metals include titanium, zirconium, niobium, tantalum and tungsten, and alloys comprising one or more such valve metals and having properties similar to those of the valve metals. Titanium is a preferred valve metal as it is readily available and relatively inexpensive when compared with the other valve metals.

25 The substrate may consist essentially of valve metal or alloy thereof, or it may comprise a core of another metal, eg steel or copper, and an outer surface of a valve metal or alloy thereof.

The outer layer of the coating of the electrode of the present invention comprises an oxide of at least ruthenium, preferably a second noble metal, and at least one suitable non-noble metal oxide. The oxide of the non-noble metal may be, for example, tantalum, zirconium, niobium, hafnium, tungsten, or preferably titanium or tin.

30 The oxide of the second noble metal, where it is present, may be, for example, an oxide of one or more of rhodium, iridium, or osmium.

The over-voltage and operational lifetime of the electrode is dependent at least to some extent on the ratio of the components in the outer layer of the coating on the electrode and on the thickness thereof. The outer layer of the coating will generally comprise at least 10 mole % in total of oxide of noble metal and at least 20 mole % of 5 oxide of non-noble metal.

In general the outer layer of the coating will be present at a loading of at least 5 g/m² of nominal electrode surface, preferably at least 10 g/m². In general it will not be necessary for the coating to be present at a loading of greater than 100 g/m², preferably not greater than 80 g/m².

10 The size of the particles in the powder charged to the plasma spray-gun, where a plasma-spray-gun is used in the process according to the present invention, is typically between 1 and 250μ, preferably between 20 and 150μ .

Where plasma-spraying is used in the process of the present invention conditions under which it can be carried out can be determined by the skilled man by simple 15 experiment. For example, in the plasma spraying system where the primary gas is argon the flow rate thereof may be between 20 and 60 standard litres per minute (slpm), or preferably between 30 and 40 slpm, where the primary gas is nitrogen the flow rate thereof may be between 20 and 60 slpm; where the secondary gas is hydrogen the flow rate thereof may be between 0 and 20 slpm, or preferably between 0 and 15 slpm, where 20 the secondary gas is helium the flow rate thereof may be between 0 and 200 slpm; where the carrier gas is argon the flow rate thereof may be between 0.1 and 10 slpm, or preferably between 1 and 4 slpm, where the carrier gas is nitrogen the flow rate thereof may be between 0.1 and 10 slpm; the torch current may be between 300 and 700 A, preferably between 400 and 650 A; and the scan speed may be between 1 and 25 1000mm/min, preferably between 350 and 600 mm/min.

Where the electrode of the present invention comprises an intermediate layer it may, for example, comprise RuO₂ and an oxide of at least one non-noble metal. The oxide of the non-noble metal may be, for example titanium dioxide, zirconium dioxide, or tantalum pentoxide or oxide of another valve metal. Alternatively, or in addition, the 30 intermediate layer may comprise an oxide of a non-noble metal other than a valve metal, and tin is an example of such a non-noble metal.

The structure of the electrode, and of the electrolytic cell in which the electrode is used, will vary depending upon the nature of the electrolytic process which is to be effected using the electrode. For example, the nature and structure of the electrolytic cell and of the electrode will vary depending upon whether the electrolytic process is one in
5 which oxygen is evolved at the electrode, eg as in an electrowinning process, an electroplating process, an electrogalvanising process or an electrotinning process, or one in which chlorine is evolved at the electrode, or one in which alkali metal chlorate or alkali metal hypochlorite is produced, as is the case where aqueous alkali metal chloride solution is electrolysed. However, as the inventive feature does not reside in the nature or
10 structure of the electrolytic cell nor of the electrode there is no necessity for the cell or the electrode to be described in any detail. Suitable types and structures of electrolytic cell and of electrodes may be selected from the prior art depending on the nature of the electrolytic process. The electrode may for example, have a foraminate structure, as in a woven or unwoven mesh, or as in a mesh formed by slitting and expanding a sheet of
15 valve metal or alloy thereof, although other electrode structures may be used.

Prior to deposition of the coating on the substrate, the substrate may be subjected to treatments which are known in the art. For example, the surface of the substrate may be roughened, for example by sand-blasting, in order to improve the adhesion of the subsequently applied coating and in order to increase the real surface area of the
20 substrate. The surface of the substrate may also be cleaned and etched, for example by contacting the substrate with an acid, eg with an aqueous solution of oxalic acid or hydrochloric acid, and the acid-treated substrate may then be washed, eg with water, and dried.

It may be necessary to repeat the thermal-spraying procedure, particularly where
25 it is a plasma-spraying procedure, one or more times in order to build up an outer layer of coating having the required loading.

According to a further aspect of the present invention there is provided an electrode which comprises a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating thereon comprising at least an outer layer of an
30 electrocatalytically-active material which comprises an oxide of at least ruthenium and an oxide of at least one non-noble metal wherein the outer layer of the coating is present at a loading of at least 5 g/m² of nominal electrode surface, preferably at least 10 g/m² and at

a loading of not greater than 100 g/m², preferably not greater than 80 g/m²; and wherein the outer layer comprises at least 10 mole % ruthenium oxide and at least 20 mole % non-noble metal oxide.

The invention is illustrated by the following Examples.

5 Examples 1-3

These Examples illustrate the preparation of electrodes according to the present invention.

General Method

A sheet of titanium was cleaned by contacting it with acetone, the cleaned sheet
10 was dried and then etched for 8 hours in 10% w/v oxalic acid at 90°C.

A powder comprising TiO₂ particles coated with RuO₂ in weight ratio 35:65, was prepared by adjusting the pH of a dispersion of TiO₂ in aqueous RuCl₃ with NH₄OH. The particles were filtered, washed, dried, milled and sieved to obtain a fraction of desired particle size (Powder A).

15 The etched sheet was coated with a sample of Powder A in a Plasma Technik 1100 system using an F4 torch under the following conditions: primary gas, argon at 36-40 litre/min; secondary gas, hydrogen at 14 litres/min; carrier gas, argon at 2.1 litres/min; current 600-650 A; injector angle 75° degrees; cooling air, on; and scan speed 500mm/min.

20 The coating procedure was repeated until a desired loading of the coating outer layer was achieved as indicated in Table 1.

TABLE 1

	Example No.	Particle Size (μ)	Loading (g/m ²)
25	1	106-250	26.1
	2	106-212	26.8
	3	106	60

In a comparative Test, a known anode comprising a coating of RuO₂/TiO₂, in weight ratio 35:65, was prepared by so-called spray-baking, ie (i) dissolving RuCl₃ (1.5gm) in pentanol (20cm³); (ii) adding Ti(O-n-Bu)₄ (6.4gm) to the solution and rolling the mixture for 1 hour to effect dissolution; (iii) applying the resulting solution to a suitably prepared substrate of titanium by spray or brush; (iv) drying the coated substrate

for 10 minutes at 180°C and baking it at 450°C for 20 minutes. Steps (iii) and (iv) were repeated until the desired coating loading was obtained.

The electrodes were tested as anodes for chlorine-producing activity by determining the anodic current onset potential (E_o) and the current density at +1.2V vs. SCE ($I_{+1.2}$) using cyclic voltammetry in a three-compartment cell, with a platinum counter-electrode. The anode potential was swept from 0 to 1.3V at 20mV/sec in saturated brine at pH 4.5 and room temperature. The results recorded on the cyclic voltammogram are shown in Table 2.

TABLE 2

	Example No.	E_o (volts)	$I_{+1.2}$ (mA/cm ²)
10	1	1.05	120
	2	1.04	180
	3	1.05	50
	CT	1.02	120

15 CT: Comparative Test

E_o : Anodic onset potential

$I_{+1.2}$: Current density at 1.2V vs. Saturated Calomel Electrode

From Table 2 it can be seen that an anode prepared by the process according to the present invention has comparable activity to a known anode.

20 Example 4

This Example illustrates a further electrode according to the present invention wherein the particles for plasma-spraying had been spray-dried.

25 A sample of Powder A, prepared in Example 1, was slurried and spray dried using a disc atomiser at a speed of 25000 rpm, with inlet and outlet temperatures of 220°C and 110°C respectively. A powder having a mean particle size of 35.9μ with a standard deviation of 48.9μ was obtained.

The procedure of Example 1 was repeated except that the current was 600A.

30 The electrode obtained thereby was tested as an anode for chlorine-producing performance and was found to have an anodic onset potential of +1.0v and a current at 1.2 V against a saturated calomel electrode of 272 mAcm⁻² revealing that it had a better catalytic performance than the anode prepared in Example 1.

Example 5

This Example illustrates an electrode according to the present invention wherein the coating comprises tin oxide and ruthenium oxide.

Ruthenium trichloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$; 54g) was dissolved in a solution of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; 193g) in concentrated HCl (100mls), the resulting solution was diluted with de-ionised water (400 cm^3) and 30%w/w NaOH was added to adjust the pH to 10. The precipitate which formed was separated from the mother liquor, washed and dried. The dried powder was sieved and a particle-size fraction of $40\text{-}150\mu$ was recovered.

The recovered fraction was plasma sprayed onto etched titanium under the conditions used in Example 1 to plasma-spray a titanium oxide/ruthenium oxide mixture except that the carrier gas (Ar) flow was 2.2 slpm instead of 2.1 slpm.

The electrode obtained thereby was tested as an anode for chlorine-producing performance and was found to have an anodic onset potential of +1.0V and a current density at 1.2 V against a saturated calomel electrode of 200 mAcm^{-2} .

Example 6

This Example illustrates an electrode according to the present invention wherein the coating comprises tin oxide, ruthenium oxide and iridium oxide.

A powder containing ruthenium oxide, iridium oxide and tin oxide in parts by weight 25/10/65 was prepared by adding $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (67.86 g) and H_2IrCl_6 (23.83 g) to a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (145.79 g) in water (600cm^3) and the pH of the resulting solution was adjusted to 10 by addition of 1M NaOH. The precipitate which formed was separated from the mother liquor, washed, dried and sieved and the fraction of particle size 0-100 microns was collected.

The aforementioned fraction was plasma-sprayed onto an etched titanium substrate using the conditions described in Example 1.

CLAIMS

1. A process for the preparation of an electrode comprising a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating thereon comprising at least an outer layer of an electrocatalytically-active material which comprises an oxide of at least ruthenium and an oxide of at least one non-noble metal which process comprises the step of thermal spraying a mixture of (i) at least ruthenium and/or oxide thereof and (ii) at least one non-noble metal and/or oxide thereof onto the substrate.
- 5 2. A process as claimed in Claim 1 wherein the thermal spraying step is a plasma-spraying step carried out in a reducing atmosphere.
- 10 3. A process as claimed in Claim 2 wherein the mixture comprises a ruthenium oxide, at least one non-noble metal oxide and at least one second noble metal oxide.
4. A process as claimed in Claim 3 wherein the at least one second noble metal oxide is an iridium oxide.
- 15 5. A process as claimed in Claim 3 wherein the at least one non-noble metal oxide is an oxide of tin or of a valve metal.
6. A process as claimed in Claim 2 wherein the substrate comprises a valve metal.
7. A process as claimed in Claim 5 or Claim 6 wherein the valve metal is titanium.
8. A process as claimed in Claim 2 wherein the size of the particles in the powder charged to the plasma spray-gun is between 1 and 250 μ .
- 20 9. A process as claimed in Claim 2 wherein where the primary gas is argon the flow rate thereof is between 20 and 60 slpm and wherein where the primary gas is nitrogen the flow rate thereof is between 20 and 60 slpm;
10. A process as claimed in Claim 2 wherein where the secondary gas is hydrogen the flow rate thereof is between 0 and 20 slpm; and wherein where the secondary gas is helium the flow rate thereof is between 0 and 200 slpm.
- 25 11. A process as claimed in Claim 2 wherein where the carrier gas is argon the flow rate thereof is between 0.1 and 10 slpm; and wherein where the carrier gas is nitrogen the flow rate thereof is between 0.1 and 10 slpm.
12. A process as claimed in Claim 2 wherein the torch current may be between 300 and 700 A.

13. A process as claimed in Claim 2 wherein the scan speed may be between 1 and 1000mm/min.
14. An electrode which comprises a substrate of a valve metal or of an alloy thereof having similar properties thereto and a coating thereon comprising at least an outer layer 5 of an electrocatalytically-active material which comprises an oxide of at least ruthenium and an oxide of at least one non-noble metal, wherein the outer layer of the coating is present at a loading of at least 5 g/m² of nominal electrode surface and at a loading of not greater than 100 g/m²; and wherein the outer layer comprises at least 10 mole % ruthenium oxide and at least 20 mole % non-noble 10 metal oxide.
15. An electrolytic cell comprising an electrode as claimed in Claim 14.
16. A process for the preparation of chlorine using an electrolytic cell as claimed in Claim 15.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/01717

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25B11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 331 528 (H.B. BEER) 25 May 1982 see column 4, line 49 - line 51 see column 5, line 13 - line 18 see column 11 - column 12; claims 33,36-40 ---	1,14
X	EP,A,0 099 866 (ENERGY CONVERSION DEVICES, INC) 1 February 1984 see page 20, line 3 - page 21, line 3 ---	1
A	DE,A,26 25 820 (TDK ELECTRONICS CO. LTD.) 30 December 1976 see page 5, line 14 - line 19 see page 9; claims 1-5,7 ---	1,3,5-7
A	FR,A,2 216 021 (SIGRI ELEKTROGRAPHIT G.M.B.H) 30 August 1974 see page 3, line 12 - line 24 -----	1

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Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4331528	25-05-82	NONE		
EP-A-0099866	01-02-84	US-A-	4537674	27-08-85
		AU-B-	567500	26-11-87
		AU-A-	1680083	26-01-84
		CA-A-	1214452	25-11-86
		JP-A-	59047390	17-03-84
DE-A-2625820	30-12-76	JP-C-	990070	18-03-80
		JP-A-	51144381	11-12-76
		JP-B-	53028279	14-08-78
		GB-A-	1508091	19-04-78
		US-A-	4061558	06-12-77
FR-A-2216021	30-08-74	DE-A-	2305175	08-08-74
		BE-A-	810444	16-05-74
		CH-A-	558677	14-02-75
		NL-A-	7316611	06-08-74